



VERIFICATION OF TRANSLATION

I, Toru Miura, of c/o SAKAI International Patent Office, 2-6, Kasumigaseki 3-chome, Chiyoda-ku, Tokyo 100-0013 Japan, hereby declare that I am a translator of the document attached, and attached document is a true and correct translation made by me to the best of my knowledge and belief.

PCT Patent Application No.PCT/JP03/05453, filed on April 28, 2003.

Signature of Translator: _____

Toru Miura

Date : January 26, 2005



(TRANSLATION)

PATENT OFFICE
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy of the following application as filed with this Office.

DATE OF APPLICATION : April 28, 2003

APPLICATION NUMBER : PCT/JP03/05453

APPLICANT(S) : Ajinomoto Co., Inc.

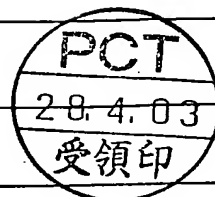
Issued : March 11, 2004

Commissioner,
Patent Office Yasuo IMAI
(Official Seal)

Certificate No. 16-500082

特許協力条約に基づく国際出願願書

原本(出願用) - 印刷日時 2003年04月28日 (28. 04. 2003) 月曜日 16時07分11秒



0	受理官庁記入欄 国際出願番号	
0-1	国際出願日	
0-3	(受付印)	
0-4	様式-PCT/RO/101 この特許協力条約に基づく国際出願願書は、 右記によって作成された。	PCT-EASY Version 2.92 (updated 01.01.2003)
0-5	申立て 出願人は、この国際出願が特許協力条約に従って処理されることを請求する。	
0-6	出願人によって指定された受理官庁	日本国特許庁 (RO/JP)
0-7	出願人又は代理人の書類記号	PAMA-15246
I	発明の名称	双頭型塩基性アミノ酸誘導体
II	出願人	出願人である (applicant only)
II-1	この欄に記載した者は	米国を除くすべての指定国 (all designated States except US)
II-2	右の指定国についての出願人である。	
II-4ja	名称	味の素株式会社
II-4en	Name	Ajinomoto Co., Inc.
II-5ja	あて名:	104-8315 日本国 東京都 中央区 京橋一丁目15番1号
II-5en	Address:	15-1, Kyobashi 1-chome Chuo-ku, Tokyo 104-8315 Japan
II-6	国籍 (国名)	日本国 JP
II-7	住所 (国名)	日本国 JP
II-8	電話番号	03-5250-8111
II-9	ファクシミリ番号	03-5250-8293
III-1	その他の出願人又は発明者	出願人及び発明者である (applicant and inventor)
III-1-1	この欄に記載した者は	米国のみ (US only)
III-1-2	右の指定国についての出願人である。	
III-1-4ja	氏名 (姓名)	英 謙二
III-1-4en	Name (LAST, First)	HANABUSA, Kenji
III-1-5ja	あて名:	386-0005 日本国 長野県 上田市 古里1918-16
III-1-5en	Address:	1918-16, Kosato Ueda-shi, Nagano 386-0005 Japan
III-1-6	国籍 (国名)	日本国 JP
III-1-7	住所 (国名)	日本国 JP

特許協力条約に基づく国際出願願書

PAMA-15246

原本(出願用) - 印刷日時 2003年04月28日 (28.04.2003) 月曜日 16時07分11秒

III-2	その他の出願人又は発明者	
III-2-1	この欄に記載した者は	出願人及び発明者である (applicant and inventor)
III-2-2	右の指定国についての出願人である。	米国のみ (US only)
III-2-4j _a	氏名(姓名)	鈴木 正浩
III-2-4e _n	Name (LAST, First)	SUZUKI, Masahiro
III-2-5j _a	あて名:	386-0017 日本国 長野県 上田市 踏入 2-16-20
III-2-5e _n	Address:	2-16-20, Fumiiri Ueda-shi, Nagano 386-0017 Japan
III-2-6	国籍(国名)	日本国 JP
III-2-7	住所(国名)	日本国 JP
IV-1	代理人又は共通の代表者、通知のあて名 下記の者は国際機関において右記のごとく出願人のために行動する。	代理人 (agent)
IV-1-1ja	氏名(姓名)	酒井 宏明
IV-1-1en	Name (LAST, First)	SAKAI, Hiroaki
IV-1-2ja	あて名:	100-0013 日本国 東京都 千代田区 霞が関三丁目2番6号 東京倶楽部ビルディング
IV-1-2en	Address:	Tokyo Club Building 2-6, Kasumigaseki 3-chome Chiyoda-ku, Tokyo 100-0013 Japan
IV-1-3	電話番号	03-5512-4699
IV-1-4	ファクシミリ番号	03-5512-4799
V	国の指定	
V-1	広域特許 (他の種類の保護又は取扱いを求める場合には括弧内に記載する。)	AP: GH GM KE LS MW MZ SD SL SZ TZ UG ZM ZW 及びハラレプロトコルと特許協力条約の締約国である他の国 EA: AM AZ BY KG KZ MD RU TJ TM 及びユーラシア特許条約と特許協力条約の締約国である他の国 EP: AT BE BG CH&LI CY CZ DE DK EE ES FI FR GB GR HU IE IT LU MC NL PT SE SI SK TR 及びヨーロッパ特許条約と特許協力条約の締約国である他の国 OA: BF BJ CF CG CI CM GA GN GQ GW ML MR NE SN TD TG 及びアフリカ知的所有権機構と特許協力条約の締約国である他の国
V-2	国内特許 (他の種類の保護又は取扱いを求める場合には括弧内に記載する。)	AE AG AL AM AT AU AZ BA BB BG BR BY BZ CA CH&LI CN CO CR CU CZ DE DK DM DZ EC EE ES FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KZ LC LK LR LS LT LU LV MA MD MG MK MN MW MX MZ NI NO NZ OM PH PL PT RO RU SC SD SE SG SK SL TJ TM TN TR TT TZ UA UG US UZ VC VN YU ZA ZM ZW

特許協力条約に基づく国際出願願書

原本(出願用) - 印刷日時 2003年04月28日 (28. 04. 2003) 月曜日 16時07分11秒

V-5	指定の確認の宣言 出願人は、上記の指定に加えて、規則4.9(b)の規定に基づき、特許協力条約のもとで認められる他の全ての国の指定を行う。ただし、V-6欄に示した国の指定を除く。出願人は、これらの追加される指定が確認を条件としていること、並びに優先日から15月が経過する前にその確認がなされない指定は、この期間の経過時に、出願人によって取り下げられたものとみなされることを宣言する。	
V-6	指定の確認から除かれる国	なし (NONE)
VI	優先権主張	なし (NONE)
VII-1	特定された国際調査機関(ISA)	日本国特許庁 (ISA/JP)
VIII	申立て	申立て数
VIII-1	発明者の特定に関する申立て	-
VIII-2	出願し及び特許を与えられる国際出願日における出願人の資格に関する申立て	-
VIII-3	先の出願の優先権を主張する国際出願日における出願人の資格に関する申立て	-
VIII-4	発明者である旨の申立て (米国を指定国とする場合)	-
VIII-5	不利にならない開示又は新規性喪失の例外に関する申立て	-
IX	照合欄	用紙の枚数
IX-1	願書 (申立てを含む)	4
IX-2	明細書	14
IX-3	請求の範囲	2
IX-4	要約	1
IX-5	図面	0
IX-7	合計	21
	添付書類	添付
IX-8	手数料計算用紙	✓
IX-17	PCT-EASYディスク	-
IX-18	その他	納付する手数料に相当する特許印紙を貼付した書面
IX-18	その他	国際事務局の口座への振込を証明する書面
IX-19	要約書とともに提示する図の番号	
IX-20	国際出願の使用言語名:	日本語
X-1	提出者の記名押印	
X-1-1	氏名(姓名)	酒井 宏明



受理官庁記入欄

10-1	国際出願として提出された書類の実際の受理の日	
------	------------------------	--

特許協力条約に基づく国際出願願書

原本（出願用） - 印刷日時 2003年04月28日（28. 04. 2003）月曜日 16時07分11秒

10-2	図面：	
10-2-1	受理された	
10-2-2	不足図面がある	
10-3	国際出願として提出された書類を補完する書類又は図面であつてその後期間内に提出されたものの実際の受理の日（訂正日）	
10-4	特許協力条約第11条(2)に基づく必要な補完の期間内の受理の日	
10-5	出願人により特定された国際調査機関	ISA/JP
10-6	調査手数料未払いにつき、国際調査機関に調査用写しを送付していない	

国際事務局記入欄

11-1	記録原本の受理の日	
------	-----------	--



DESCRIPTION

TANDEM TYPE BASIC AMINO ACID DERIVATIVES

Technical Field

The present invention relates to tandem type basic amino acid derivatives which are useful for gelling or solidifying various organic medium, etc. which is liquid at ambient temperature and also relates to a gelling agent or a solidifying agent containing at least one of them.

Background Art

A method where fluidity of various kinds of cosmetics/perfumeries, pharmaceuticals, agricultural chemicals, adhesives, resins, paints, etc. which are liquid at ambient temperature is controlled so as to process into a form being fit for the purpose of diversified uses is a very important art in industry. In addition, disaster and marine pollution by accident caused by spilled oil are becoming severe social problems but, if oil is able to be solidified, it is possible not only to prevent diffusion of oil but also to easily and efficiently recover it and a gelling treatment of spilled oil is able to be a very effective means for prevention of spilled oil. Moreover, waste edible oil coming out from ordinary households is a cause for the pollution of quality

of water and, if the waste oil can be gelled by a simple method and discarded as a solid, its harmful influence on environment is able to be reduced.

With regard to a substance having a function of controlling the fluidity and viscosity of liquid substances as such, there have been known alkaline metal salts of long-chain fatty acids (Patent Document 1: JP-A-55-75493), metal soaps (Patent Document 2: JP-B-59-52196), 12-hydroxystearic acid (Patent Document 3: JP-B-60-44968), condensates of polyhydric alcohols with benzaldehyde (Patent Document 4: JP-A-59-77859), N-acylamino acid amides (Patent Document 5: JP-B-54-33798), etc.

Among them, alkaline metal salts of long-chain fatty acids and metal soaps required much adding amount for gelling or solidifying the liquid organic medium, and further restricted the condition for use such as pH. In addition, with regard to 12-hydroxystearic acid, types of organic medium being able to be solidified are little and gelling ability thereof is low as well and, therefore, the resulting gel has weak strength, is fragile and is apt to be crumbled whereupon it is insufficient in terms of stability of the gel around ambient temperature. On the other hand, although condensates of polyhydric alcohols with benzaldehyde represented by dibenzylidene sorbitol are able to make many organic media into gel, there is a restriction in the joint use with a low-boiling

substance or a substance which is not so resistant to heat because their dissolving temperature is high. In addition, there is a disadvantage that the acetal moiety in the condensate is unstable and is decomposed. Although N-acylamino acid amides represented by N-lauroyl-L-glutamic acid α,γ -di-n-butylamide are able to gel or solidify many organic media in small adding amount and strength of the resulting gel is high as well, their gelling ability to lower alcohol such as methanol is poor and they do not always have a satisfactory gelling ability.

In order to improve the disadvantages as mentioned above, development of gelling agents or solidifying agents for organic media has been briskly carried out in recent years. Examples thereof are cyclohexane tricarboxamide (Patent Document 6: JP-A-10-273477), bis(acylamino)cyclohexane derivatives (Patent Document 7: JP-A-10-237034), oligopeptide alkylamide derivatives (Patent Document 8: JP-A-10-245396; Patent Document 9: JP-A-10-226614), dialkylurea derivatives prepared by the reaction of diaminocyclohexane with alkyl isocyanate (Patent Document 10: JP-A-8-231942), cyclic dipeptides (Patent Document 11: JP-A-7-247474); Patent Document 12: JP-A-7-247473), N^α -alkyl or alkenylcarbamoyl- N^0 -acylamino acid ester compounds (Patent Document 13: JP-A-2000-256303), etc. They are able to gel or solidify various kinds of liquid organic media in small

additional amount, strength of the resulting gel is strong and stability around the ambient temperature is good as well. On the other hand however, gelling ability is greatly affected by steric configuration of the compound whereby synthesis and separation of the material having a specific steric configuration are difficult, availability of the material is difficult or, in the manufacture, there are many reaction steps and the process is complicated whereby there is a problem in productivity.

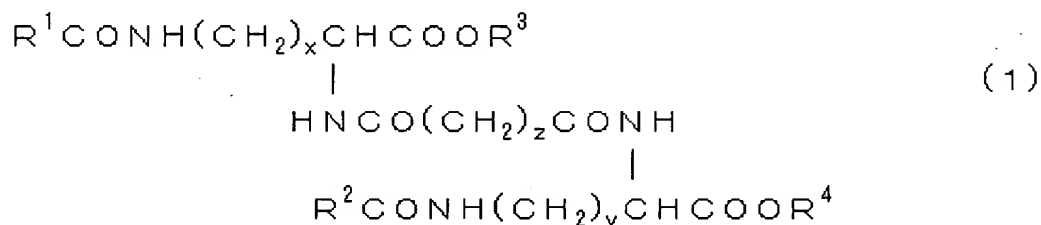
Further, N^α-alkyl or alkenylcarbamoyl-N^ω-acylamino acid ester compounds (Patent Document 13: JP-A-2000-256303) are disclosed as gelling agents or solidifying agents for varieties of organic media such as lower alcohol, chlorine-type solvents or hydrocarbon oils. Even by them however, there is a variation in the gelling ability depending upon the type of the organic medium such as that, as compared with hydrocarbon oil, the gelling ability for lower alcohol or chlorine-type solvent is low.

Disclosure of the Invention

Matters to be solved by the present invention is to provide a gelling agent or a solidifying agent which is able to gel or solidify various kinds of liquid organic media in a small adding amount and which is also able to be manufactured easily.

The present inventors have carried out extensive investigations for solving the above-mentioned problems and found that the basic amino acid derivative represented by the following formula (1) has an excellent gelling ability to various kinds of liquid organic media and is also able to be manufactured easily whereupon the present invention has been achieved. Thus, the present invention is as follows.

[1] A basic amino acid derivative represented by the following formula (1).



(In the formula,

R^1 and R^2 each independently is a straight-chain or branched-chain alkyl or alkenyl group having 5 to 21 carbon atoms,

R^3 and R^4 each independently is an alkyl or alkenyl group having 1 to 22 carbon atom(s) or hydrogen atom in which the alkyl or alkenyl group may be either in straight-chain or branched-chain or may have a cyclic structure,

z is an integer of 0 or more and

x and y each is an integer of 2 to 4.)

[2] The basic amino acid derivative according to the above [1], wherein z in the above formula (1) is 0 to 10.

[3] The basic amino acid derivative according to the above [1] or [2], wherein z in the above formula (1) is 0.

[4] The basic amino acid derivative according to any one of the above [1] to [3], wherein R^1 and R^2 each in the above formula (1) is a straight-chain alkyl group having 11 carbon atoms.

[5] A gelling agent or a solidifying agent of an organic medium which is characterized in containing at least one member of the basic amino acid derivative mentioned in the above [1] to [4].

Best Mode for Carrying Out the Invention

The present invention provides a basic amino acid derivative represented by the above formula (1), and a gelling agent or a solidifying agent in which the above is an effective ingredient. Incidentally, the compound represented by the above formula (1) may also be called a tandem type basic amino acid derivative.

R^1 and R^2 each independently is a straight-chain or branched-chain alkyl or alkenyl group having 5 to 21 carbon atoms. The carbon atom numbers of R^1 and R^2 each are preferably 7 to 11.

R^3 and R^4 each independently is an alkyl or alkenyl group having 1 to 22 carbon atom(s) or hydrogen atom. Structure of the above alkyl or alkenyl group may be either in straight-chain

or branched-chain or may have a cyclic structure. In view of a gelling ability, it is preferred to be in a branched structure while, in the case of a straight chain, there is a tendency that the less the carbon numbers, the better.

z is an integer of 0 or more, preferably 0 to 10 and, particularly preferably, 0.

The tandem type basic amino acid derivative of the present invention may be synthesized by a generally known common methods using the above-mentioned N^o-acylamino acid, alcohol and fatty acid chloride having carboxyl groups at both ends as starting materials. For example, it is able to be synthesized by such a manner that esterification of a carboxylic acid moiety of the N^o-acylamino acid is firstly carried out according to an esterification reaction such as a dehydrating condensation upon heating (at ordinary pressure or *in vacuo*), a transesterification reaction or an azeotropic dehydrating condensation reaction with an alcohol either in the presence or absence of a catalyst and then the resulting N^o-acylamino acid ester compound is made to react with a one-half equivalent of a fatty acid chloride having carboxyl groups at both ends in an inert solvent in the presence or absence of a catalyst. Instead of the above method, it is of course possible to conduct a method where an N^o-acylamino acid is firstly made to react with a fatty acid chloride having carboxyl groups at both ends and then the product is esterified.

It is further acceptable that the substance is not esterified.

In some cases, unreacted materials in addition to the desired ester compound may remain in the reaction product prepared as such and the product may be purified by known methods such as extraction, recrystallization and chromatography. When there is no influence on a gelling ability, the product in a state of the mixture *per se* may be used.

Examples of the N^0 -acylamino acid are N^{ϵ} -acyllysine, N^{δ} -acylornithine and N^{γ} -acyl- α,γ -diaminobutyric acid and, among them, N^{ϵ} -acyllysine is most preferred.

With regard to the acyl group (R^1 and R^2) in the N^0 -acylamino acid, that which is derived from a straight-chain or branched-chain and saturated or unsaturated fatty acid having 5 to 21 carbon atoms is preferred and its examples are long-chain acyl groups derived from octanoic acid, decanoic acid, lauric acid, palmitic acid, stearic acid, oleic acid, etc. When carbon numbers of the acyl group are 22 or more, a gelling ability becomes poor in some cases and that is not adequate.

The N^0 -acylamino acid may be easily synthesized by, for example, subjecting a basic amino acid and a long-chain fatty acid to dehydration by heating. An example of the commercially available N^0 -acylamino acid is Amihope LL (N^{ϵ} -lauroyl-L-lysine) manufactured by Ajinomoto.

The N⁰-acylamino acid may be either an optically active substance or a racemic substance and, in view of an improvement in a gelling ability, the optically active substance is preferred. In addition, it may be used either solely or two or more thereof may be used as a mixture.

The alcohol (R³ and R⁴) used for esterification of N⁰-acylamino acid is a saturated or unsaturated and straight-chain, branched-chain and/or cyclic alcohol having 1 to 22 carbon(s) and its examples are methanol, ethanol, n-propanol, isopropanol, n-butanol, 2-butanol, n-pentanol, n-hexanol, cyclohexanol, n-heptanol, n-octanol, 2-ethylhexanol, n-nonanol, n-decanol, lauryl alcohol, myristyl alcohol, palmityl alcohol, stearyl alcohol, oleyl alcohol, stearyl alcohol, isostearyl alcohol, behenyl alcohol and 2-octyldodecanol. It is also possible that no esterification is conducted. When carbon numbers are more than 22, the resulting gelling ability may be poor in some cases and that is not adequate.

There is no particular limitation for a dicarboxylic acid chloride which is used for the reaction of two molecules of N⁰-acylamino acid alkyl ester with a fatty acid chloride having carboxyl groups at both ends and its examples are oxalyl chloride, malonyl chloride, succinyl chloride, glutaryl chloride, adipoyl chloride, pimeloyl chloride, suberoyl chloride, azelaoyl chloride, sebacoyl chloride and

dodecanedioyl chloride. That where carbon number(s) (z) of the methylene chain is/are 0 to 10 is preferred and that where it is 0 is most preferred. It may be used either solely or two or more thereof may be used as a mixture.

The present invention further provides a gelling agent or a solidifying agent where the tandem type basic amino acid derivative is an effective ingredient. In the gelling agent or solidifying agent of the present invention, it is sufficient that at least one member of the above-mentioned tandem type basic amino acid derivative of the present invention is used as an effective ingredient and the case where two or more thereof are mixed is acceptable as well. It is also possible that other gelling agent or solidifying agent is added to the gelling agent or solidifying agent of the present invention so far as that does not deteriorate the advantage of the present invention. Examples of other gelling agent or solidifying agent are N-acyl-L-glutamic acid dialkylamide, polyamide resin, 1,2-hydroxystearic acid, sodium stearate, dibenzylidene-D-sorbitol and fatty acid dextrin. The gelling agent or solidifying agent of the present invention may also contain other components such as substrate material and auxiliary agent. Examples of other components are surface-active agent, additive and powder.

Examples of the surface-active agents are anionic surface-active agent such as N-long-chain acylamino acid salt

(e.g., N-long-chain acyl acidic amino acid salt and N-long-chain acyl neutral amino acid salt), N-long-chain fatty acid acyl-N-methyltaurine salt, alkyl sulfate and alkylene oxide adduct thereof, fatty acid amide ether sulfate, fatty acid metal salt and weakly basic salt, sulfosuccinate-type surface-active agent, alkyl phosphate and alkylene oxide adduct thereof and alkyl ether carboxylic acid; nonionic surface-active agent such as ether-type surface-active agent (e.g., glycerol ether and alkylene oxide adduct thereof), ester-type surface-active agent (e.g., glycerol ester and alkylene oxide adduct thereof), ether-ester-type surface-active agent (e.g., sorbitan ester and alkylene oxide adduct thereof), ester-type surface-active agent (e.g., polyoxyalkylene fatty acid ester, glycerol ester, fatty acid polyglycerol ester, sorbitan ester and sucrose fatty acid ester), nonionic surface-active agent of a nitrogen-containing type (e.g., alkylglucoside, hydrogenated castor oil pyroglutamic acid ester and ethylene oxide adduct thereof and fatty acid alkanolamide); cationic surface-active agent (e.g., aliphatic amine salt including alkylammonium chloride and dialkylammonium chloride), quaternary ammonium salt thereof, aromatic quaternary ammonium salt including benzalkonium salt and fatty acid acylarginine ester; and amphoteric surface-active agent such as betaine-type surface-active agent (e.g., carboxybetaine), aminocarboxylic

acid-type surface-active agent and imidazoline-type surface-active agent; etc.

Examples of various additives are amino acid such as glycine, L-alanine, DL-alanine, serine, threonine, arginine, glutamic acid, aspartic acid, leucine and valine; polyhydric alcohol such as glycerol, ethylene glycol, 1,3-butylene glycol, propylene glycol and isoprene glycol; water-soluble polymer such as polyamino acid including polyglutamic acid and polyaspartic acid as well as salt thereof, polyethylene glycol, acacia, alginate, xanthan gum, hyaluronic acid, hyaluronate, chitin, chitosan, water-soluble chitin, carboxyvinyl polymer, carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyltrimethylammonium chloride, poly(dimethylmethylenepiperidium chloride), quaternary ammonium salt of polyvinylpiperidone derivative, cationized protein, decomposed collagen and derivative thereof, acylated protein and polyglycerol; sugar alcohol such as mannitol and alkylene oxide adduct thereof; and lower alcohol such as ethanol and propanol. Still more examples are animal and plant extracts, nucleic acid, vitamin, enzyme, anti-inflammatory agent, bactericide, antiseptic, antioxidant, ultraviolet-absorber, chelating agent, antiperspirant, pigment, dye, oxidation dye, organic and inorganic powders, pH-adjusting agent, pearling agent and moisturizer.

Examples of various powders are resin powder such as

Nylon beads and silicone beads, Nylon powder, metal fatty acid soap, yellow iron oxide, red iron oxide, black iron oxide, chromium oxide, cobalt oxide, carbon black, ultramarine blue, Prussian blue, zinc oxide, titanium oxide, zirconium oxide, silicon oxide, aluminum oxide, cerium oxide, mica titanium, boron nitride, barium sulfate, calcium carbonate, magnesium carbonate, aluminum silicate, magnesium silicate, silicon carbide, pigment, lake, sericite, mica, talc, kaolin, barium sulfate with a plate shape, barium sulfate with a butterfly shape, fine particles of titanium oxide, fine particles of zinc oxide, fine particles of iron oxide and acylamino acid such as acyllysine, acylglutamic acid, acylarginine and acylglycine. Those which are subjected to a surface treatment such as treatment with silicone, with a fluorine compound, with a silane coupling agent, with silane and an organic titanate, with an acylated lysine, with a fatty acid, with a metal soap, with an oil and with an amino acid may be acceptable as well.

The basic amino acid derivative of the present invention has an excellent action of gelling or solidifying various kinds of liquid organic media by addition of small amount thereof. Examples of the liquid organic media mentioned here are mineral oil such as gasoline, kerosene, light oil and heavy oil; animal oil such as whale oil and herring oil; plant oil such as soybean oil, olive oil, castor oil, linseed oil, corn oil, sunflower oil, rapeseed oil and cotton seed oil; hydrocarbon such as

petroleum benzin, liquid paraffin, benzene, toluene, hexane and cyclohexane; ester such as ethyl acetate, butyl acetate, amyl acetate, diethyl sebacate, dioctyl sebacate, diethyl phthalate, dioctyl phthalate and polyoxyalkylene glycol fatty acid ester; ether such as diglyme and polyalkylene glycol ether; cyclic ether such as THF and dioxane; ketone and aldehyde such as acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone and anisaldehyde; lower alcohol such as methanol, ethanol, propanol and butanol; silicone oil such as methyl polysiloxane, methylphenyl polysiloxane, octamethyl cyclotetrasiloxane and decamethyl cyclopentasiloxane; halogen such as chlorobenzene and carbon tetrachloride; and highly polar organic solvent such as DMF and DMSO. Thus, the present invention is effective to a very wide range of organic media regardless of combustible and incombustible and is also effective to a medium where such organic media are mixed or are main components.

When the basic amino acid derivative of the present invention is added to a liquid organic medium, heated with stirring, if necessary, at about 50 to 120°C so as to give a homogeneous state and allowed to stand at ambient temperature, it is possible to prepare a gelled or solidified product. Although it depends on the type of an organic medium to be gelled or solidified, amount of the compound of the present invention used therefor is 1 to 400 part(s) by weight, preferably 1 to

200 part(s) by weight, more preferably 1 to 100 part(s) by weight or, still more preferably, 2 to 80 parts by weight to 1,000 parts by weight of the liquid organic medium. When the amount used is less than 1 part by weight, a sufficient gelling is not achieved while, when it is more than 400 parts by weight, a part of the gelling agent is crystallized and separated out upon gelling and, therefore, a non-homogeneous state is resulted, appearance is not good and stable gel strength is unable to be maintained whereupon that is not appropriate. Incidentally, hardness of the solidified product can be freely adjusted by the adding amount of the compound of the present invention.

Accordingly, the tandem type basic amino acid derivative of the present invention is able to be synthesized by a simple method from an easily available material which is industrially manufactured. When the tandem type basic amino acid derivative of the present invention is added to perfumery/cosmetic, pharmaceutical, agricultural chemical, adhesive, resin, paint, etc. containing the above-mentioned organic medium, it is possible to control the fluidity thereof.

Examples

The present invention will now be specifically illustrated by way of the following examples although the present invention is not limited thereto.

[Manufacturing Example 1] Synthesis of
bis(N^ε-lauroyl-L-lysine)oxalyl amide

N^ε-Lauroyl-L-lysine (Amihope LL; manufactured by Ajinomoto) (19.71 g, 60 mmol) was dissolved in 600 ml of a 2 wt% aqueous solution of NaOH and ethyl ether was added thereto. Freshly distilled oxalyl chloride (3.81 g, 30 mmol) was slowly added to the ether layer. The two-layered solution was stirred for about 1 hour by keeping at 0°C and, after that, it was stirred for 23 hours at room temperature. The resulting white precipitate was filtered, well washed with water and dried. The resulting crude product was purified by recrystallizing twice from methanol-ether. Its data by elementary analysis, IR, NMR, etc. supported the structure. Result of the IR measurement is shown below.

Result of IR measurement (KBr): 3317, 1733, 1661, 1640, 1541 cm⁻¹

[Manufacturing Example 2] Synthesis of
bis(N^ε-lauroyl-L-lysine-2-ethylhexyl)oxalyl amide

N^ε-Lauroyl-L-lysine (20 g, 0.061 mol), 9.54 ml (0.061 mol) of 2-ethylhexanol and 23.2 g (0.122 mol) of p-toluenesulfonic acid monohydrate were heated to reflux together with 300 ml of benzene for two days using a Dean-Stark apparatus where temperature of an oil bath was kept at 130°C. The residue prepared by a vacuum evaporation of excessive benzene was dissolved in 100 ml of THF, 32 g/32 ml (0.230 ml)

of morpholine were added thereto and the mixture was stirred. Insoluble matters were filtered and the filtrate was allowed to stand in a refrigerator for about 1 hour. This was filtered and concentrated *in vacuo*, diethyl ether was added thereto followed by shaking and such an operation was repeated twice. That was concentrated *in vacuo* and the resulting residue was dried to give 22.04 g of solid.

The above solid (12.3 g) was dissolved in 200 ml of dehydrated THF. To this added were 30 ml (0.014 mol) of dehydrated triethylamine. Under ice-cooling, 2 ml (0.028 mol) of oxalyl chloride were added thereto followed by being allowed to stand for one night at room temperature. The insoluble triethylamine hydrochloride was removed by means of a natural filtration and the filtrate was concentrated *in vacuo*. The resulting crude product was recrystallized from methanol and diethyl ether to give bis(N^ε-lauroyl-L-lysine-2-ethylhexyl)oxalyl amide.

Result of IR measurement (KBr): 3293, 1736, 1646, 1522
cm⁻¹

[Manufacturing Example 3] Synthesis of
bis(N^ε-lauroyl-L-lysine-3,5,5-trimethylhexylethyl)oxalyl
amide

It is able to be synthesized by nearly the same method as in Manufacturing Example 2.

Result of IR measurement (KBr): 3319, 3278, 1741, 1662,

1642, 1538 cm^{-1}

Test Method 1

The compounds of the present invention each was precisely weighed and added to a test tube equipped with a cover, 1 ml of an organic medium was added thereto, the cover was closed and the mixture was heated until the mixture was homogeneously dissolved. After being dissolved, it was allowed to stand for 2 hours in a constant-temperature bath of 25°C and the state was observed by naked eye. When a gelling was incomplete, the compound was added while, when a completely gelling was noted, the organic medium was added whereupon the minimum amount (mg) of the compound necessary for gelling of each organic medium per ml was determined. However, the maximum amount of the compound which was able to be added was set at 200 mg to 2 ml of the organic medium and the case where the state was liquid or crystals were separated out was evaluated as "not gelled".

Evaluation:

When the amount of a gelling agent necessary for gelling 1 ml of an organic medium was 25 mg or less, it was evaluated as oo; when the amount was 26 to 35 mg, it was evaluated as o; when the amount was 36 to 45 mg, it was evaluated as Δ ; and when the amount was 46 mg or more, it was evaluated as x.

Table 1

Liquid Organic Medium	Example 1	Example 2	Example 1	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
	Compound of Manufacturing Example 1	Compound of Manufacturing Example 2	Compound of Manufacturing Example 3	12-Hydroxy stearic acid	Lauroyl-L-glutamic acid dibutyl amide	N ^ε -Octadecyl carbamoyl-N ^α -lauroyl-lysine methyl ester	N ^ε -Octadecyl carbamoyl-N ^α -lauroyl-lysine ethyl ester
Methanol	Δ	oo	oo	not gelled	not gelled	oo	×
Benzene	o	oo	oo	—	oo	Δ	o
DMF	o	o	o	not gelled	×	o	Δ
DMSO	oo	oo	oo	not gelled	×	oo	oo
CCl ₄	oo	oo	Δ	oo	Δ	×	×

It is apparent from Table 1 that, as compared with the conventional gelling agents, addition of small amount of the tandem type basic amino acid derivatives of the present invention is able to gel various kinds of organic media.

Industrial Applicability

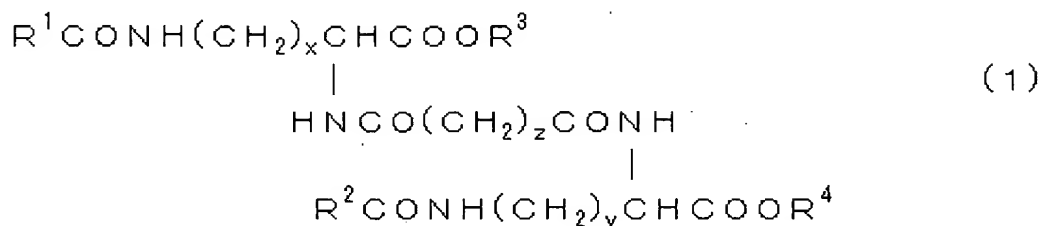
In accordance with the present invention, it is now possible that various kinds of liquid organic media are able to be gelled or solidified using a small adding amount of the tandem type basic amino acid derivative represented by the above formula (1). According to the present invention, it is also possible to provide a gelling agent or a solidifying agent which is able to be synthesized by a simple method. In addition, a gelled product formed by the use of the tandem type basic amino acid derivative of the present invention has an excellent stability for a long period around the ambient temperature.

In the production and processing of a product group including liquid organic media being exemplified by perfumeries/cosmetics, pharmaceuticals, agricultural chemicals, adhesives, resins, paints, etc. which are liquid, the present invention is useful for the control of fluidity of the liquid organic media and for the processing into a form being fit for the purpose of diversified uses. Further, the present invention is preferably applicable in the field of environmental preservation such as a gelling treatment of

spilled oil in the sea and a gelling treatment of waste oil coming out of ordinary households.

Claims

1. A basic amino acid derivative represented by the following formula (1).



(In the formula,

R^1 and R^2 each independently is a straight-chain or branched-chain alkyl or alkenyl group having 5 to 21 carbon atoms,

R^3 and R^4 each independently is an alkyl or alkenyl group having 1 to 22 carbon atom(s) or hydrogen atom in which the alkyl or alkenyl group may be either in straight-chain or branched-chain or may have a cyclic structure,

z is an integer of 0 or more and

x and y each is an integer of 2 to 4.)

2. The basic amino acid derivative according to claim 1, wherein z in the above formula (1) is 0 to 10.

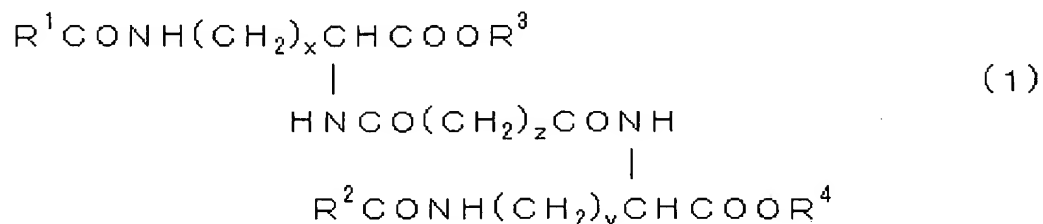
3. The basic amino acid according to claim 1 or 2, wherein z in the above formula (1) is 0.

4. The basic amino acid derivative according to any one of claims 1 to 3, wherein R^1 and R^2 each in the above formula (1) is a straight-chain alkyl group having 11 carbon atoms.

5. A gelling agent or a solidifying agent of an organic medium which is characterized in containing at least one member of the basic amino acid derivative mentioned in claims 1 to 4.

Abstract

The present invention provides a novel basic amino acid derivative represented by the following formula (1).



(In the formula, R^1 and R^2 each independently is a straight-chain or branched-chain alkyl or alkenyl group having 5 to 21 carbon atoms; R^3 and R^4 each independently is an alkyl or alkenyl group having 1 to 22 carbon atom(s), hydrogen atom in which the alkyl or alkenyl group may be either in straight-chain or branched-chain or may have a cyclic structure; z is an integer of 0 or more; and x and y each is an integer of 2 to 4.)

In accordance with the basic amino acid derivative of the present invention, its small adding amount is able to gel or solidify various kinds of liquid organic media whereupon there is provided a gelling agent or a solidifying agent being easily synthesized by a simple method and giving a gelled product being excellent stability for a long period at ambient temperature.